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**Porosity of Hardened
Portland Cement Pastes**

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Porosity of Hardened Portland Cement Pastes*

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SYNOPSIS

Continued study of the properties of hardened portland cement pastes has provided information which makes it possible to estimate porosity of pastes more precisely than is possible by using the original equations of Powers and Brownyard. The total pore volume of hardened pastes is $0.99 w_e$. Capillary pore volume is the difference between total pore volume and pore volume characteristic of the gel in hardened pastes.

The pore volume of the gel is assumed to be the lowest pore volume that has been observed in hardened pastes. The paste with the lowest pore volume was made with $w_o/c = 0.235$ and cured for 11 years. The gel porosity calculated for this paste is 0.26. The average number of layers of water molecules on the surface of this saturated gel is 2.38.

INTRODUCTION

Definitions of symbols

α = nonevaporable water per gram of cement in a completely hydrated paste	v_t = apparent specific volume of the total water
c = weight of cement	\bar{V}_w = partial specific volume of water
d_p = density of a saturated hardened paste	V_m = weight of water required to form an adsorbed monolayer over the surface in a hardened paste
ϵ = porosity of hardened paste	V_p = volume of paste
k = ratio of V_m to w_n	w_e = weight of evaporable water in the hardened paste
p_c = capillary pore volume in hardened paste	w_n = weight of nonevaporable water in the hardened paste
p_g = gel pore volume in hardened paste	w_t = weight of total water in the hardened paste
p_t = total pore volume in hardened paste	
v^o = specific volume of pure water	
v_c = specific volume of cement	
v_h = specific volume of hydration products	

General relationships

The fact that a hardened portland cement paste that is saturated with water can lose all of its evaporable water with only a slight change in volume implies that the hardened paste is porous. A study of relationships between the properties and porosities of hardened pastes led Powers and Brownyard¹ to conclude that there are two classes of pores: (1) gel pores—small pores between the gel particles, and (2) capillary pores—pores larger than gel pores which exist between aggregates of gel particles.

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Some of the physical properties of a hardened paste, the permeability to water for example, depend upon the total porosity; other properties, such as compressive strength and resistance to freezing, are related to the capillary porosity. Therefore, an accurate equation for capillary porosity is necessary to evaluate precisely the effect of capillary and gel porosities upon the properties of the paste.

Some of the details of the Powers and Brownyard model have been changed as a result of continued research. We have found that their equation for calculating capillary porosity gives negative values in a few instances; consequently, the problem of computing the porosity from certain readily measured properties of the paste has been studied further so as to understand the cause for the negative results and to obtain a more accurate equation.

The equation for calculating capillary pore volume, p_c , given by Powers and Brownyard, is

$$p_c = w_o - v_t (1 + nk) w_n \dots \dots \dots (1)$$

where w_o is the original net* water content of the fresh paste, w_n is the non-evaporable water content of the saturated, hardened paste, v_t is the minimum value of the apparent specific volume of the total water that can exist in saturated pastes, n is the average number of layers of water in the gel pores, and k is the ratio of the amount of water necessary to form a monolayer on the gel to the nonevaporable water content of the paste.

The apparent specific volume of water in hardened paste is the difference between the volume of the paste and the volume of the cement it contains divided by the weight of water, both free and chemically combined, in the paste. That is

$$v_t = \frac{\bar{V}_p - cv_c}{w_t}$$

The partial specific volume of the water is the rate of change of volume of the paste with respect to the change in the weight of water it contains at a constant cement content, and nonevaporable water content

$$\bar{V}_w = \left(\frac{\partial V_p}{\partial w_e} \right)_{c, w_n}$$

We investigated each of the factors in Eq. (1) and found that the porosity of the gel is considerably smaller than was estimated from the pastes available to Powers and Brownyard. In addition, discovery that the partial specific volume of evaporable water in saturated pastes is constant² suggested a simpler basis than that used previously for calculating porosity. The total pore volume of a hardened paste is equal to the volume of the solution held by its pores when the paste is saturated. This volume can be estimated from the total water content and the partial specific volume of the water in saturated pastes. The gel pore volume can be estimated in the same manner from pastes

*Corrected for bleeding, if any.

which contain no capillary pores. The capillary pore volume is simply the difference between the total and gel pore volumes.

EXPERIMENTAL PROCEDURES

Materials

Pastes were prepared from five different cements covering a wide range of cement compositions. The computed potential compound compositions of the cements are given in Table 1.

Preparation of samples

The pastes used in this investigation were, with the exceptions noted below, mixed in a vacuum by the method described in a previous paper.³ Since the pastes so prepared were free from air bubbles, their water contents could be determined accurately from simple drying or ignition procedures.

The pastes were cured under water at 73 F, in closed glass molds.

Some of the results considered here were obtained upon pastes prepared for other projects. Although curing procedures varied, care was exercised to include only the results obtained on saturated pastes. The samples may be separated into three groups:

Group 1—These specimens were prepared for permeability studies. There is evidence that some leaching of lime and alkali occurred during the permeability test.

Group 2—These pastes were prepared to determine the relationship between the specific surface and the nonevaporable water over as great a range in nonevaporable water as possible.

Group 3—A series of specimens were prepared in 1940 in accordance with the procedure used for autoclave tests of cements. The specimens were cured in a moist closet during the first 24 hr and under water at 73 F until analyzed at the end of 11 years. Water-cement ratios ranged from 0.215 to 0.25 by weight.

These pastes were not vacuum mixed. Freshly broken surfaces of the specimens appeared wet, indicating that the specimens were saturated. Little leaching occurred during the 11-year curing period. This was shown by comparing the chemical analysis of the cured paste with the original analysis of the cement.

TABLE 1—PROPERTIES OF CEMENTS USED IN POROSITY INVESTIGATION

Cement lot No.	Specific surface of cement (Wagner), sq cm per g	Specific volume of cement, cu cm per g	Loss on ignition, percent	Computed potential compound composition, percent				
				C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄
15754	1800	0.319	0.95	45.0	27.7	13.4	6.7	4.0
15756	1800	0.315	1.39	48.6	27.9	4.7	12.6	2.9
15758	1800	0.322	1.56	60.6	11.6	10.2	7.7	3.2
15761	1800	0.317	0.40	44.9	29.2	9.8	7.5	3.1
15763	1800	0.311	0.74	33.5	53.6	2.3	6.0	3.2

Analytical methods

The total water content, w_t , of saturated, hardened pastes prepared by the vacuum mixing procedures was calculated directly from the ignition loss, at 1900 F, of the paste. A correction for the original ignition loss of the cement was made. (When the pastes contained air voids, the total water content was found from the sum of nonevaporable water and evaporable water, the latter being determined by the procedure described by Powers and Brownyard.⁴)

The densities, d_p , of the saturated pastes prepared by the vacuum mixing procedure were determined by a specific gravity balance. This determination was made upon the sample before it was crushed and dried for other tests. For pastes of group 3, the density determination was performed on samples which were granulated to eliminate voids. The grinding was done in a controlled atmosphere cabinet where the air was saturated with water and free of CO₂.

Nonevaporable water in the samples, w_n , was determined from the ignition loss at 1900 F of samples dried in an evacuated desiccator connected to a trap cooled by dry ice and alcohol.⁵

From the density and total water content of vacuum-mixed, saturated specimens it is possible to calculate original water content, w_o , assuming that no over-all volume change occurs during the hydration period. Let c and w_t represent the weight of the cement and total water, respectively, in the hardened paste. Then

$$d_p = \frac{c + w_t}{cv_c + w_tv_t} \dots\dots\dots(2)$$

where v_c and v_t are the specific volume of the cement and apparent specific volume of the total water, respectively, and d_p is the paste density. If the volume does not change during the hydration period

$$cv_c + w_tv_t = cv_c + w_ov^o \dots\dots\dots(3)$$

where w_o is the original water content and v^o is the specific volume of chemically free water. From Eq. (2) and (3)

$$\frac{w_o}{c} v^o = \frac{1 + w_t/c}{d_p} - v_c \dots\dots\dots(4)$$

The volume occupied by the original water is given by the right-hand member of Eq. (4); v^o is 0.99,² so that the weight ratio, w_o/c , is readily determined.

The specific areas of the pastes were estimated from water-adsorption measurements. The amounts of water ad-

sorbed at four different relative vapor pressures were determined by measuring the weight increase of samples, dried to the nonevaporable water state, suspended from silica springs in glass jackets. Each jacket was evacuated after the introduction of the sample, then connected to a ves-

TABLE 2—RELATIVE VAPOR PRESSURES OVER SATURATED SOLUTIONS OF COMPOUNDS USED FOR RELATIVE VAPOR PRESSURE CONTROL

NaOH·H ₂ O	0.0703
LiCl·H ₂ O	0.1105
K(C ₂ H ₃ O ₂)·1.5H ₂ O	0.2245
MgCl ₂ ·6H ₂ O	0.3300

sel containing a saturated solution of a pure compound. The four compounds and the relative vapor pressures over their saturated solutions are listed in Table 2.

The two parameters, V_m and C , of the BET adsorption equation⁶ were calculated from adsorption data. V_m is the amount of water necessary to form a complete monolayer over the surface, and C is related to the average heat of adsorption in the first layer.

DISCUSSION

Total pore volume in hardened pastes

Powers and Brownyard determined the specific volume of the solid phases in hardened pastes by a helium-displacement method and obtained the volume of pores from the difference between over-all volume and volume of the solid phases. Then from the mass of water in saturated samples they concluded that water in gel pores had a smaller specific volume than water in capillary pores. The difference between the specific volume of gel and capillary water complicated the calculation of porosity of pastes. In an investigation reported in another paper we found, by a water-displacement method, that partial specific volume of gel water is equal to that of capillary water in saturated pastes.² This simplifies determination of the total pore volume in hardened pastes.

The pores of a saturated paste are filled with a solution of soluble cement constituents, principally alkalis, in chemically free water. We cannot determine directly the density of this solution, but we have determined that partial specific volume of chemically free water in pastes made from certain low-alkali cements is 0.99. It is not likely that variations in cement composition, including variations in alkali content, will affect this value appreciably. Consequently, we can use it to approximate closely the volume of the solution in the pores of hardened pastes by calculating the volume occupied by chemically free water in saturated paste. This approximation has been applied to solutions of KOH and NaOH in the range of concentrations to be expected in hardened pastes. The difference between approximated volume and true volume of the solution is less than 0.5 percent. Even if the concentration of alkali in the evaporable water were twice the probable highest concentration, the error would be below 1 percent. We believe, therefore, that the error in pore volume associated with this approximation is less than 0.5 percent. The evaporable water content is assumed to be equal to the chemically free water content of hardened pastes.

In other words, within 0.5 percent, the total pore volume, p_t , of a hardened paste is equal to the weight of evaporable water in the saturated paste multiplied by 0.99, *i.e.*,

$$p_t = 0.99w_e = 0.99(w_t - w_n) \dots \dots \dots (5)$$

Since the water gained by the paste during the curing period is given by

$$w_t - w_o = 0.254w_n \text{ (Ref. 2)}$$

TABLE 3—MEAN *k* VALUES FOR
VARIOUS CEMENTS

Cement No.	<i>k</i>
15754	0.310
15756	0.348
15758	0.310
15761	0.317
15763	0.374

it follows that
 $p_t = 0.99(w_o - 0.746w_n)$

Gel pore volume

Powers and Brownyard concluded that the framework of a hardened paste was a gel which possessed its own characteristic porosity. They had evidence that the gel pores could hold a quantity of water equal to $4V_m$,

or the equivalent, $4kw_n$. The term *n* of Eq. (1) was thus assigned the value of 4 by Powers and Brownyard.

When the procedure for determining w_n was revised,⁵ it became necessary to investigate again the relationship between V_m and w_n . The later work shows that V_m is proportional to w_n in pastes made from cements with normal C_2S and C_3S contents, but V_m may not be exactly proportional to w_n in pastes made from cements with high C_2S contents. Since the departure from proportionality is small, even if real, we shall ignore it, and use the values of *k* reported in Table 3 for different cements. These values are different from those reported by Powers and Brownyard because of the difference in the method of determining w_n . The relationship between V_m and w_n will be discussed in more detail in another paper.

The proportionality of V_m to w_n implies that the specific surface of the hydration products is a constant and is independent of the extent of hydration of the cement in the paste. Apparently, gel particles do not grow larger as hydration proceeds; but new particles, similar in size to those first formed, are produced. It seems reasonable to suppose that a mechanism that produces gel particles of fairly uniform size should also produce a fairly uniform mode of packing these particles; consequently, the gel would possess a characteristic porosity.

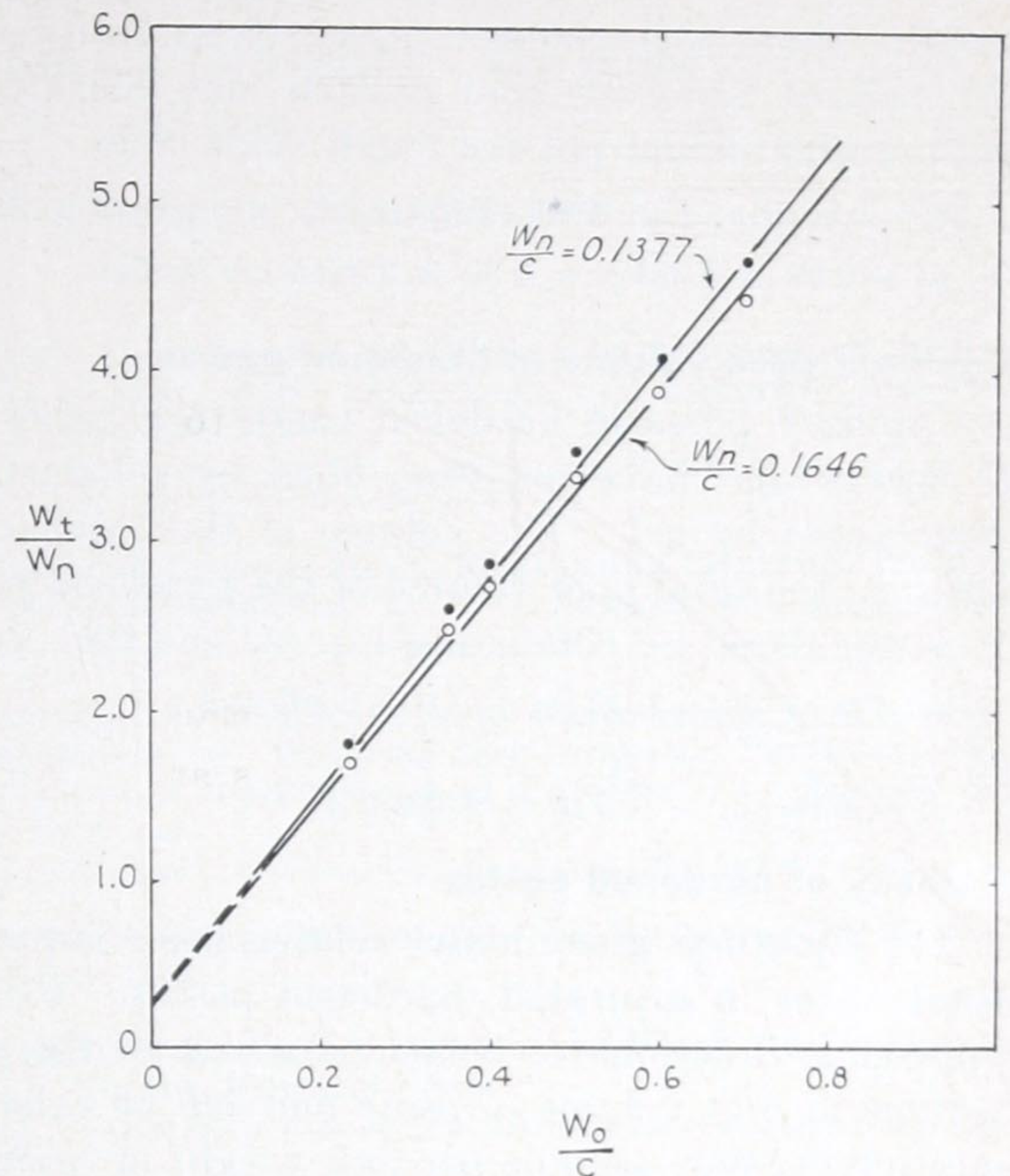
The minimum value of the ratio w_e/V_m for hardened pastes is a measure of gel porosity, for pores of saturated hardened paste are filled with evaporable water; and surface area, which is proportional to V_m , is due to colloidal hydration products comprising the gel. The lowest value of w_e/V_m found for pastes investigated in this work is 2.38. We have not been able to establish the minimum value, although the proportionality between V_m and w_n implies that a gel porosity corresponding to $w_e/V_m \geq 1$ must exist.

The general results we have obtained in attempting to determine a minimum value for w_e/V_m are illustrated by the following consideration:
Since

$$\frac{w_e}{V_m} = \frac{w_t - w_n}{kw_n} = \left(\frac{w_t}{w_n} - 1\right) \frac{1}{k} \dots\dots\dots (6)$$

it follows that if a lower limit for w_e/V_m exists, a lower limit for w_t/w_n must also exist. In a saturated paste w_t/w_n is related to the original water-cement ratio, w_o/c , by the equation:²

Fig. 1— $\frac{w_t}{w_n} - \frac{w_o}{c}$ relationship
for pastes of cement 15754
at two $\frac{w_n}{c}$ levels



$$\frac{w_t}{w_n} = \frac{w_o/c}{w_n/c} + 0.254 \dots \dots \dots (7)$$

From Eq. (7) we should expect then that the ratio w_t/w_n for saturated, hardened pastes having the same w_n/c would lie on a straight line when plotted against w_o/c . The intercept of this line at $w_o/c=0$ should be 0.254, and the slope $1/(w_n/c)$. Fig. 1 is a plot of two sets of data. These data were obtained on pastes at ages up to 11 years. The points are close to the theoretical lines and show no break, indicating that the minimum w_t/w_n has not been reached.

The lowest values of w_t/w_n were reached after 11 years; it is not likely that values appreciably lower than these will ever be reached. It will probably be necessary to deduce the minimum values of w_t/w_n and w_e/V_m from other types of measurements.

The porosity, ϵ , of a hardened paste containing neither unhydrated cement nor capillary pores is

$$\epsilon = \frac{0.99w_e}{v_h \left(1 + \frac{1}{\alpha} \right) w_n + 0.99w_e} = \frac{w_e/V_m}{\frac{v_h \left(1 + \frac{1}{\alpha} \right)}{0.99k} + \frac{w_e}{V_m}} \dots \dots \dots (8)$$

where v_h is the specific volume of the hydration products and α is the maximum value of w_n/c . Porosities calculated from Eq. (8) with $w_e/V_m=2.38$ range from 0.26 to 0.28 for the cements studied here. These porosities are close to that characteristic of a close-packed system of uniformly sized spheres, 0.26. Inequality of particle size in a close-packed system could lead to porosities

smaller than 0.26 and consequently to ratios of w_e/V_m smaller than 2.38. We believe, however, that particle size distribution in gels is narrow; thus, gel porosity should not fall much below 0.26.

Accordingly, the best estimation of p_g now possible is given by

$$p_g = 0.99 \times 2.38V_m = 0.99 \times 2.38kw_n = 2.36kw_n \dots \dots \dots (9)$$

Capillary pore volume in hardened pastes

Capillary pores in hardened pastes are larger than gel pores. They exist as spaces that have not been filled by gel particles and may be completely surrounded by gel. The volume of the capillary pores, p_c , is the difference between the total pore volume of the hardened paste and the gel-pore volume. It is calculated by combining Eq. (5) and (9).

$$p_c = p_t - p_g = 0.99 [w_t - (1 + 2.38k)w_n] \dots \dots \dots (10)$$

or

$$p_c = 0.99 [w_o - (0.746 + 2.38k)w_n]$$

Porosity of hardened pastes

The equations given above relate pore volume to nonevaporable water and total water in saturated, hardened pastes. Usually these quantities are expressed as fractions of cement content of the pastes. Porosity is the pore volume in unit volume of paste and can be calculated from w_n/c and w_t/c by multiplying pore volume per unit weight of cement by amount of cement in a unit volume of paste. The equations for total and capillary porosity are:

$$\epsilon = \frac{p_t}{V_p} = 0.99 \left[\frac{w_t}{c} - \frac{w_n}{c} \right] \frac{d_p}{1 + \frac{w_t}{c}} \dots \dots \dots (11)$$

$$\frac{p_c}{V_p} = 0.99 \left[\frac{w_t}{c} - (1 + 2.38k) \frac{w_n}{c} \right] \frac{d_p}{1 + \frac{w_t}{c}} \dots \dots \dots (12)$$

where d_p is the density and V_p is the volume of the paste.

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For such discussion of this paper as may develop please see Part 2, December 1956 JOURNAL. In Proceedings V. 52 discussion immediately follows the June 1956 JOURNAL pages.

**Bulletins Published by the
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